PATENT SPECIFICATION

DRAWINGS ATTACHED

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COMPLETE SPECIFICATION

The Preparation of Organic Isocyanates

We, FARBENFABRIKEN BAYER AKTIENGESELLSCHAFT, of Leverkusen-Bayerwerk, Germany, a body corporate organised under the laws of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the preparation of organic isocyanates, and more particularly to an improved method for preparing alkyl, cycloalkyl, alkaryl, aralkyl, aryl, cycloaliphatic and heterocyclic, mono- and poly-isocyanates from an amine and phosgene.

It has heretofore been proposed to prepare organic isocyanates by reacting phosgene with an amine. This process is generally carried out in two steps (see, for example, the process disclosed by W. Siefkin, Liebigs, Annalen der Chemie, Volume 563 (1949) page 96 *et seq*). The first step of this reaction known as the "cold phosgenation" step may be carried out by preparing a solution or suspension of an amine in an inert solvent and mixing this solution or suspension with an excess of phosgene. In this step of the reaction it is necessary to maintain the temperature of the mixture substantially below 60° C. to prevent the production of unwanted side reaction products, such as disubstituted ureas. Because of the exothermic reaction between the phosgene and the amine, the maintenance of the temperature below 60° C. necessitates cooling the reaction mixture artificially. In this first step of the reaction the amine is converted to a mixture of carbamyl chloride and amine hydrochloride. Upon a subsequent treatment at higher temperatures with a further excess of phosgene, the carbamyl chloride and hydrochloride are converted into the isocyanate corresponding to the original amine component. This subsequent treatment or "hot phosgenation" step is carried out at elevated temperatures above the decomposition point of the carbamyl chloride.

It is known that the intensity of stirring in the first reaction stage has an influence on the yield of isocyanate per unit of volume and time. In British Patent Specification No. 761,590 it has been proposed to use a turbo-mixer or a circulating pump, such as a centrifugal pump, as a mixing member. This process of mixing the amine solution with a solution of phosgene in such a pump permits the use of amine solutions of high concentration and results in high yields of isocyanate. However, a process such as this is dependent on the capacity of the pump.

According to the above-mentioned British patent specification, it is necessary to prepare a solution or a suspension of an amine, which is supplied simultaneously with phosgene or a solution of phosgene in a solvent to a circulating pump or turbomixer, the residence time of the amine solution or suspension in the mixer being between a few seconds and one minute. This residence time imposes a limit upon the amount of amine which can be converted to isocyanate within a given period of time.

Another method of carrying out the cold phase phosgenation step is set forth in British Specification No. 763,535. According to this specification, there is claimed a process of manufacturing organic isocyanates from organic amines and phosgene, the step which includes passing an inert solvent solution of an amine into an organic solvent solution of phosgene, at least 1.25 mols of phosgene being present per equivalent $-NH_2$ group of the amine, the reaction being conducted under superatmospheric pressure and under conditions of turbulent flow while maintaining the temperature above that at which the carbamyl chloride of the particular amine employed is decomposed.

No matter what procedure is followed in the cold phosgenation step, the carbamyl

chloride and amine hydrochloride formed in the first step is subsequently heated to a temperature of at least 100° C. and generally between 100° C. and 200° C. in the second or hot phosgenation step, while introducing additional phosgene to convert the carbamyl chloride and hydrochloride into the corresponding isocyanate.

The present invention provides a process for the production of organic isocyanates by reacting an organic amine under pressure in a mixing zone with phosgene, wherein one of the components (phosgene or amine) follows a spiral path and the other component is introduced into the vortex in counter-current in a primary phosgenation step to produce the corresponding carbamyl chloride and amine hydrochloride, which is reacted in a second phosgenation step with a further excess of phosgene at a temperature of at least 100° C. to produce the corresponding isocyanate.

After the preliminary phosgenation step, it is advantageous to remove the mixture by way of an outlet helix as this causes a reduction in, or even counterbalances, the swirling motion and thus reduces the loss in pressure in the mixing zone.

A method of mixing the two components, phosgene and amine, under pressure in accordance with the present invention is shown in the accompanying drawings, in which:—

Figure 1 is a cross-sectional view of one type of mixer;

Figure 2 is a sectional view along the lines II—II of Figure 1, and

Figure 3 is a cross-sectional view of another embodiment of a mixing apparatus useful in this invention in which the ingredients are mixed in two distinct and separate stages.

In Figure 1, one of the components, which may be either the organic amine or the phosgene, is fed by means of a pipe line 1 into an inlet helix 2. The component may, or may not be dissolved in a suitable solvent as desired. The component then enters the apex of a conical chamber 3 and is caused to move in a swirling motion due to the inlet helix 2. The swirling motion of this component causes it to spiral down the conical internal wall surface of the chamber 3 toward an outlet helix shown generally at 5. The second component enters the chamber 3 in the opposite direction to component one by passing through an inlet 4 in the base of the hollow cone. This second component may be dissolved in a suitable solvent if desired. The second component is introduced into the core of the vortex formed by the whirling motion of the liquid resulting from the co-operation between the inlet helix 2 and the walls of the chamber 3. The introduction under pressure effects the intimate mixing of the phosgene and the organic amine and thus results in the rapid reaction of the components to form the corresponding carbamyl chloride and hydrochloride. The initial pressure with which the components enter into the chamber 3, causes the mixed solution which is rapidly spinning in a spiral path, due to the walls of the chamber 3, to enter the outlet helix 5.

This outlet helix 5 causes the turbulent flow to be smoothed out and preserves some of the pressure necessary for generating the vortex in the apparatus. The helix 5 can have the same form as indicated in Fig. 2 for the inlet helix 2, but operating in the opposite sense to that shown in Fig. 2. As the solution continues to spin, it reaches the junction point of the helix 5 with an outlet or discharge conduit 6 from whence it passes to the apparatus which carries out the hot phosgenation step of the process, (not shown). Of course, any apparatus which is suitable for carrying out the hot phase phosgenation step may be used in conjunction with the process of the present invention.

By the method of this invention it is also possible for example, for the amine and the solvent to be brought together by separate pipes at a point immediately prior to entering the reaction zone. This can be done in a premixing apparatus which intimately mixes the solvent and amine before being introduced into the main mixing zone where the phosgene and the amine are contacted. Of course, it is to be understood that a premixing device of this sort may be utilised not only for the organic amine, but also to mix the phosgene with a solvent. An apparatus of this type is illustrated in Figure 3 of the accompanying drawings. A counter-current mixing chamber 3 is exactly the same as shown in Figure 1 and operates in the same manner as described for Figure 1, however, the conduit 4 of Figure 1 has been replaced with a premixing chamber 7 which includes a first inlet conduit 8, a second inlet conduit 9 and an inlet helix 10. The chamber 7 together with the inlet means and the helix 10 permits the rapid mixing of one of the components with a suitable solvent. In operation, the amine for example, enters by way of conduit 9 and the solvent by way of conduit 8. The amine solution is caused to follow a helical path and spiral down the length of the chamber 7. The solvent is introduced into the core of helix and thus causes the intimate mixing of the two. This solution is then introduced directly into the vortex of the spiralling phosgene solution in the main mixing chamber 3 where intimate mixing with the phosgene solution occurs in the manner described above.

In the process of the present invention the components are introduced in counter-current to each other and under pressure. The components may be introduced in the reaction

chamber under any desired high pressures because the chamber itself serves as a pressure relieving member. It is preferred, however, that the components are introduced under a pressure of from 0.1 atmospheres to 15 atmospheres gauge. As a result of the pressure under which the reaction components are introduced, the throughput over a given period of time and for a given size reaction chamber is exceptionally high. The process of this invention is also advantageous in that no moving parts are contained in the mixing device. Also, an increase in the rate of conversion of organic amine to the corresponding organic isocyanate results without any loss in yield. The process eases the problem of handling the amine and phosgene since a series of mixing chambers may be combined in the manner set forth in Figure 3 thus eliminating any pipes, pumps, valves or separate chambers for storing and conveying the solvent and the reaction components to the mixing chamber. The elimination of these additional pieces of apparatus is of great technical value in view of the severe toxicity and the high vapour pressure of phosgene.

The process of the invention is also particularly advantageous for the reason that no temperature control is necessary in the primary phosgenation step as is necessary in the processes of the prior art. For example, in the method of this invention the temperature in the mixing chamber may be permitted to rise as high as 200° C. It is preferred, however, that the temperature within the mixing chamber is maintained at from 50 to 130° C. Although the temperature may be higher than that which the prior art states as being maximum for the primary phosgenation step, the yield of isocyanate produced by the method of this invention is not adversely effected by these temperatures. The disubstituted urea by-products do not result in a decrease in the yield of isocyanates even when temperatures as high as 200° C. are used in the phosgenation step. It is believed that these high temperatures can be tolerated because of the rapidity with which the organic amine is intimately mixed with the phosgene thus preventing the formation of disubstituted ureas.

It is, of course, to be understood that the phosgene may enter either end of the reaction chamber as long as it enters the end opposed to that by which the amine is introduced. Further, the phosgene solution is preferably cooled to from −5° C. to 30° C. prior to its entrance into the reaction chamber.

The period of time or the residence time of the solution in the counter-current mixing chamber in accordance with this invention varies from 0.001 to 0.1 second and preferably from 0.005 to 0.05 second. It can readily be seen comparing the residence time of the method of this invention with the residence time of the methods set forth in the aforementioned two patents that the method herein disclosed results in a greater increase in quantity of isocyanate and yield per unit of time and per unit size of reaction chamber. According to the method of the present invention, organic amines with or without the solvent may be used in the reaction with phosgene. It is preferred, however, that the concentration of amine in the solvent is from 3% to 30%.

The method of this invention is applicable for the preparation of any organic isocyanate such as, alkyl, cycloalkyl, alkaryl, aralkyl, heterocyclic and aryl, mono-, and polyisocyanates. The isocyanates are useful as intermediates in producing many valuable materials. For example, they may be reacted with organic compounds having active hydrogen-containing groups in the molecule (for example, hydroxyl-containing polyesters and polyesteramides, polyhydric polyalkylene ethers and thioethers and polyacetals) to produce polyurethanes in the form of cellular or elastomeric products. The cellular products are useful as insulating materials, seat cushions and pillows. The elastomeric materials are useful as automobile tyres, valve buttons, diaphragms, gears, accumulator bladders and bellows.

Illustrative examples of isocyanates, which may be prepared in accordance with the process of the present invention, by reaction of phosgene with the corresponding primary amine, are hexyl isocyanate from hexylamine; octyl isocyanate from octylamine dodecyl isocyanate from dodecylamine; octadecyl isocyanate from octadecylamine; tetramethylene diisocyanate from tetramethylenediamine; pentamethylene diisocyanate from pentamethylene diamine; hexamethylene diisocyanate from hexamethylenediamine; octamethylene diisocyanate from octamethylenediamine; undecamethylene diisocyanate from undecamethylene diamine; dodecamethylene diisocyanate from dodecamethylenediamine; 3,3'-diisocyanato dipropylether from 3,3'-diaminodipropylether; cyclohexyl isocyanate from cyclohexylamine; tetrahydro-α-naphthyl isocyanate from tetrahydro-α-naphthylamine; tetrahydro-β-naphthyl isocyanate from tetrahydro-β-naphthylamine, etc.; xylylene diisocyanates from xylylenediamines; diphenylmethane-4,4'-diisocyanate from 4,4'-diaminodiphenylmethane; β,β-diphenylpropane-4,4'-diisocyante from 4,4' - diamino - β,β'-diphenylpropane; benzyl isocyanate from benzylamine; phenylethyl isocyanate from phenylethylamine; p - isocyanatobenzyl isocyanate from *p* - amino - benzylamine; phenyl isocyanate from aniline; *o*-chlorophenyl isocyanate from *o*-chloroaniline; *m*-chlorophenyl isocyanate from *m*-chloroaniline; *p*-ethoxyphenyl isocyanate from *p*-ethoxyphenylamine; *p*-methoxyphenyl isocyanate

from *p*- anisidine; *p*-cetylphenyl isocyanate from *p*-cetylaniline; *p*-dodecylphenyl isocyanate from *p*-dodecylaniline; 5-dodecyl-2-methylphenyl isocyanate from 5-dodecyl-*o*-toluidine; 3-nitro-4-dodecyl phenyl isocyanate from 3-nitro-4-dodecyl aniline; *p*-cetyloxyphenyl isocyanate from *p*-cetyloxyaniline; metaphenylene diisocyanate from metaphenylenediamine; *p*-phenylene diisocyanate from *p*-phenylenediamine; 1-methylphenylene-2,4-diisocyanate from 1-methylphenylene-2,4-diamine; naphthylene-1,4-diisocyanate from 1,4-naphthylene diamine; 2,6-toluylene diisocyanate from 2,6-toluylenediamine; 1,3,5-benzene-triisocyanate from 1,3,5-benzene-triamine; 2,4,4'-triisocyanato-diphenylether from 2,4,4'-triaminodiphenyl ether; and tetrahydrofurfuryl isocyanate from tetrahydrofurfurylamine.

Any suitable solvent or suspension agent may be used in the primary phosgenation step for example, benzene, toluene, xylenes, chlorobenzene, dichlorobenzenes, tetrahydronaphthalene, chlorotoluenes, chlorinated aromatic hydrocarbons, nitrobenzene, cyclohexane, kerosene, benzine, carbon tetrachloride, tetrachlorethylene, trichlorethylene, amylbenzene, *o*-, *m*-, and *p*-cymenes, dodecylbenzene, naphthalene, heptylcyclopentane, diphenyl, chlorinated diphenyls, heptane, dioxane, dibutylether and diisobutyl ketone. The concentration of the amine and the phosgene in the chosen solvent(s) depends on the starting materials used. However, it is preferred that the concentration of the organic amine in the solvent is from 3% to 30% and the concentration of the phosgene in the solvent from 5% to 50%.

The present invention is further illustrated by the following examples, in which parts are given by weight unless otherwise specified:—

EXAMPLE 1

A solution of 275 parts of a mixture of 2,4- and 2,6-toluylene-diamines and 3000 parts of *o*-dichlorobenzene is heated to 150° C. and fed by means of a pump into the inlet 4 of Figure 1 of the accompanying drawings. In the same way, the outer vortex 1 of the chamber is simultaneously charged with a phosgene solution obtained from 1000 parts of phosgene and 3200 parts of *o*-dichlorobenzene, the solution being cooled to 0° C. The volume of the mixing chamber is 25 cc. With an initial pressure of 6 atmospheres gauge on the phosgene solution side and 4 atmospheres gauge on the amine solution side, a total of 3 cubic metres per hour passes through the chamber. The temperature which is obtained directly following the passage through the chamber is 105° C. By after-treatment with phosgene for 2 hours at a temperature of 160° C. toluylene diisocyanate is obtained with a yield of 96.0% determined by distillation.

EXAMPLE 2

400 parts of 4,4'-diaminodiphenylmethane, dissolved in 2600 parts of chlorobenzene are reacted as described in Example 1 in a chamber having a capacity of 25 cc., with 1000 parts of phosgene dissolved in 2600 parts of chlorobenzene. The amine solution entering the inlet 4 is heated to 125° C. and the initial pressure is 2.2 atmospheres gauge while the throughflow velocity is 1.5 cubic metres per hour. On the phosgene solution side, a temperature of −5° C., an initial pressure of 5.0 atmospheres gauge and a throughput of 1.5 cubic metres per hour were measured. After passing through the chamber, the temperature is 90° C. The conversion of the amine into isocyanate is completed by an after-treatment with phosgene at 120° C., this treatment lasting for 2 hours.

The concentrate obtained after distilling off chlorobenzene contains only 1.9 parts of undistillable residue to 100 parts of 4,4'-diisocyanatodiphenyl-methane. The yield is consequently more than 98% of the theoretical.

EXAMPLE 3

As described in Example 1, a solution at a temperature of 20° C. and consisting of 500 parts of *m*-chloroaniline in 2200 parts of chlorobenzene are fed through a counter-current mixing chamber with an initial pressure of 5.5 atmospheres gauge and a throughput of 1.7 cubic metres per hour. A solution cooled to −4° C. and consisting of 660 parts of phosgene in 2800 parts of chlorobenzene is supplied with an initial pressure of 6.5 atmospheres gauge and a throughput of 1.7 cubic metres per hour. The temperature of the mixture obtained is 48° C. The mixture is in the form of a suspension which can be satisfactorily stirred and is initially heated over a period of 3 hours to 110° C. and after-treated with phosgene for another 2 hours at this temperature. The yield of *m*-chlorophenyl isocyanate after working up by fractional distillation is 95.2% of the theoretical.

EXAMPLE 4

For the production of stearyl isocyanate from stearyl-amine a mixing chamber as shown in Fig. 1 with a capacity of 25 cc. is used. The pipeline 1 is charged with a solution of 590 parts of phosgene in 2350 parts of chlorobenzene. The temperature is +2° C., the initial pressure is 6.0 atmospheres gauge and the throughput 1.8 cubic metres per hour. 1.6 cubic metres of a solution heated to 90° C. and consisting of 770 parts of stearylamine in 2000 parts of chlorobenzene is hourly introduced through the inner vortex 4 with an initial pressure of 4.4 atmospheres gauge. The reaction mixture leaving the chamber at

a temperature of 88° C. is a thin liquid and substantially clear. It is after-treated for 2 hours at 120° C. with phosgene and thereafter worked up by distillation. From 100 parts of concentrate free from solvent, it is possible to distil out 97 parts of stearyl isocyanate. As residue, there remain 3 parts of a blackish-brown tar.

EXAMPLE 5

A solution of 265 parts of hexamethylene diamine in 2700 parts of *o*-dichlorobenzene and at a temperature of 20° C. is introduced at a throughput velocity of 0.8 cubic metres per hour into the pipeline 1 of a counter-current mixing chamber as shown in Fig. 1 with a capacity of 20 ccs. In contrast to Examples 1 to 4, the phosgene solution consisting of 690 parts of phosgene and 3100 parts of *o*-dichlorobenzene is introduced into the inlet 4 of the mixing chamber. The temperature of the phosgene solution is −5° C. and that of the mixture immediately beyond the chamber is 80° C. The product is after-treated for 10 hours with phosgene at 160° C. and thereafter distilled. The yield of hexamethylene diisocyanate is 93.6% of the theoretical.

EXAMPLE 6

A solution of 300 parts of 1,3-bis(amino-methyl)-benzene in 3000 parts of chlorobenzene is conducted through a counter-current mixing chamber as shown in Fig. 1 with a solution of 900 parts of phosgene in 3000 parts of chlorobenzene as in Example 5. The amine solution, which is supplied to the pipeline 1 of the chamber, is under an initial pressure of 2.4 atmospheres gauge and is cooled to −5° C., while the phosgene solution is under a pressure of 2.2 atmospheres gauge and has a temperature of −10° C. The throughput velocities reach values of 1.2 cubic metres per hour for amine solution and phosgene solution. Beyond the mixing chamber a temperature of +144° C. is measured. The after-treatment with phosgene at 105° C. lasts 20 hours and the yield of 1,3-bis-(isocyanatomethyl)-benzene is 94.9% of the theoretical, calculated on reacted amine.

WHAT WE CLAIM IS:—

1. A process for the production of organic isocyanates by reacting an organic amine under pressure in a mixing zone with phosgene, wherein one of the components (phosgene or amine) follows a spiral path and the other component is introduced into the vortex in counter-current in a primary phosgenation step to produce the corresponding carbamyl chloride and amine hydrochloride, which is reacted in a second phosgenation step with a further excess of phosgene at a temperature of at least 100° C. to produce the corresponding isocyanate.

2. A process as claimed in Claim 1, wherein one of the components (phosgene or amine) enters the mixing zone in a substantially spiral pattern at a gauge pressure of from 0.1 to 15 atmospheres and the other component is introduced into the vortex of said spiral pattern under a gauge pressure of from 0.1 to 15 atmospheres.

3. A process as claimed in Claims 1 or 2, wherein the organic amine and the phosgene are each dissolved in an inert solvent.

4. A process as claimed in Claim 3, wherein the phosgene and amine are each separately mixed with an inert solvent immediately prior to entering the mixing zone.

5. A process as claimed in Claims 1 to 4, wherein the temperature within the mixing zone is maintained between 50° C. and 130° C.

6. A process as claimed in Claims 1 to 5, wherein the phosgene solution is cooled to between −5° C. and 30° C. prior to entering the reaction chamber.

7. A process as claimed in Claims 1 to 6, substantially as hereinbefore described with reference to any of the examples and the accompanying drawings.

8. Organic isocyanates when produced by a process as claimed in any of the preceding claims.

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901,377 COMPLETE SPECIFICATION

1 SHEET

This drawing is a reproduction of the Original on a reduced scale.

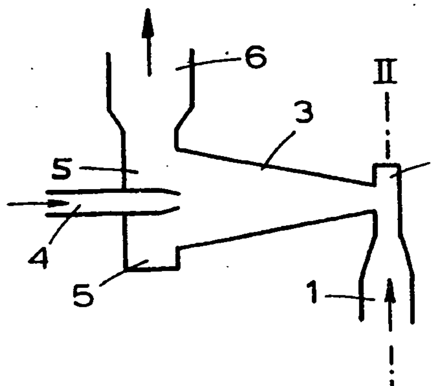

FIG.1.

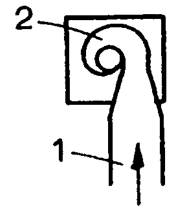

FIG.2.

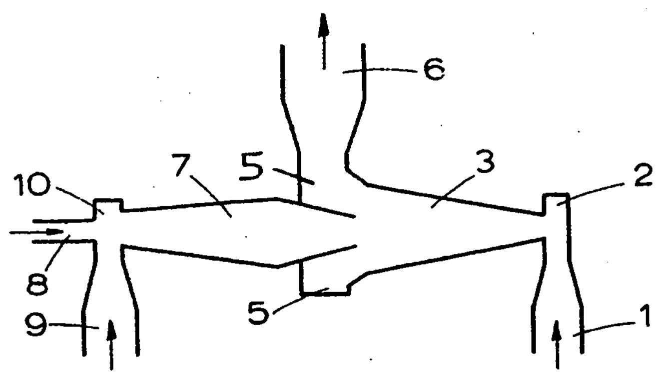

FIG.3